XXIIId-1.

STRUCTURAL ASPECTS OF THE METAL-INSULATOR TRANSITIONS IN TITANIUM AND VANADIUM OXIDES.

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Most of the compounds which have temperature induced metal-insulator transitions are oxides of titanium and vanadium. In order to determine the nature of the distortions and the variation of the thermal vibrations that take place at these transitions, we have determined the crystal structure of the metallic and insulating phases of VO_2 + 2.4% Cr, VO_2 and the Magneli phases, Ti_4O_7 and V_4O_7. In VO_2 + 2.4% Cr the metallic phase has the rutile structure, whereas the insulating one has a monoclinic distortion, which is different from the monoclinic distortion of pure VO_2 (J. M. Longo and P. Kierkegaard, Acta Chem. Scand. 24, 420 (1970)). In the insulating phase of VO_2 + 2.4% Cr half of the vanadium atoms are paired along the pseudo rutile c axis, while the other half form zig-zag chains along the same axis. This contrasts with VO_2, where in the insulating phase all the vanadium atoms are paired. The root mean square thermal displacements of the metallic rutile phase of VO_2 + 2.4% Cr are anomalously large when compared with the insulating phase or the rutile phases of TiO_2 and CrO_2. This indicates that there is a substantial lattice contribution to the entropy change at the metal-insulator transition. Ti_4O_7 undergoes two closely spaced metal-insulator transitions at ~ 150°K and ~ 125°K (R. F. Bartholomew and D. R. Frankl, Phys. Rev. 187, 828 (1969)). Structural refinements performed at 298, 140, and 120°K show that the Ti^{3+} and Ti^{4+} atoms are ordered at 120°K, whereas they are completely disordered at 298°K. This is the first clear crystallographic evidence for charge localization at a metal-insulator transition. The ordering consists of chains of Ti^{3+} cations which are paired along the pseudo rutile c axis and adjacent Ti^{4+} chains running with a zig-zag pattern along the same axis. These chains break at the crystallographic shear plane such that the two titanium atoms across the shared octahedral face are Ti^{3+} and Ti^{4+}, respectively. Although there is a large decrease in both the magnetic susceptibility (L. N. Mulay and W. J. Danley, J. Appl. Phys. 41, 877 (1970)) and electrical conductivity at the 150°K transition, there is no marked change in interatomic distances. The root mean square thermal displacements at 140°K are anomalously large compared to their counterparts at either 298°K or 120°K. The structural changes that take place in V_4O_7 at the metal-insulator transition will also be discussed.

XXIIId-2.

STRUCTURE OF MOLTEN STATE ALUMINA.

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Because, in general, the diffraction patterns of molten materials show only very weak halos, especially at very high temperatures, in contrast with strong and sharp peaks by crystalline materials, the focussing diffraction geometry which gives strong diffraction is often required in order to collect the data by a counter diffractometer.

In the present study, the structure of molten state alumina (Al_2O_3) at 2200°C in inert atmosphere was investigated by the radial distribution function analysis. The diffraction data were collected with MoKα and CuKα radiations monochromatized by a graphite monochromator. The diffraction apparatus used was a stationary specimen powder diffractometer attached with a high temperature furnace attainable up to 2500°C.

The surface tension usually makes difficult to keep the surface of molten specimen flat. In this study, therefore, this difficulty was avoided by using a specially devised molybdenum ribbon specimen holder which serves, at the same time, as the heater.

The difference radial distribution function and the radial distribution function were computed and the structure of molten alumina was compared with the structure of corundom, β-alumina, alumina gel etc. It was found that the structure of molten alumina resembles that of alumina gel, although Al-O distance observed was slightly extended.

XXIIId-3.

PRESSURE-INDUCED ELECTRONIC AND STRUCTURAL TRANSFORMATION IN SOME RARE EARTH MONOCHALCOGENIDES.

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The rare earth monochalcogenides crystallize in NaCl-type structure and are metallic or semiconducting depending on whether the rare earth ion is in a trivalent or a divalent state. Recent measurements of the electrical resistivity as a function of pressure (Jayaraman et al. Phys. Rev.Lett. (1970), 25, 368; (1970), 25, 1430) have shown a continuous semiconductor-metal (SM) transition in SmSe and SmTe and a discontinuous transition in SmS. These involve promotion of the 4f-electrons in the rare earth ion to the 5d-conduction band and a consequent conversion of the divalent ions to a trivalent state. We present in this paper, the results of the high pressure X-ray diffraction studies on the chalcogenides of Sm, Eu and Yb. A diamond anvil camera upto 300 kbar and a tungsten-carbide anvil camera upto 50 kbar have been used with silver and sodium chloride as pressure markers. The pressure-volume relations determined from the variation of the lattice parameter with pressure, are anomalous near SM-transition and exhibit large volume change. We attribute this to the conversion under pressure of the divalent ions to the smaller trivalent ions. Further, PrTe, SmTe and EuTe exhibit NaCl-CsCl type transition in the 100 kbar-range.